

3.0 CORROSION CHEMISTRY

Water is used as a moderator and heat transfer medium in Light Water Reactors (LWR) nuclear plants. If the chemistry of water is not carefully controlled, exposure of metal to water leads to corrosion.

In LWR, the corrosion rates are extremely low; nevertheless, corrosion and the formation of corrosion products is a very important consideration. The interdependence of corrosion control with chemical processes in a reactor system is shown in Figure 3.1-1.

Corrosion is a gradual chemical or electrochemical attack in a metal by its surroundings such that the metal is converted into an oxide, salt or other compound.

It is convenient to represent many common varieties of corrosion by one or more of five general reactions: These reactions are:

- Combination of metals with non metals (no water)
$$M_e + N_m = M_e N_m$$
- Combination of metals with oxygen (in presence of water)
$$M_e + 1/2 O_2 + H_2O = M_e(OH)_2$$
- Displacement of hydrogen from an acid or acid solution
$$M_e + H_2SO_4 \rightarrow M_e SO_4 + H_2$$
- Displacement of hydrogen from water
$$M_e + H_2O \rightarrow M_e(OH)_2 + H_2$$
- Displacement of one metal with another
$$M_e' + M_e SO_4 \rightarrow M_e' SO_4 + M_e$$

Corrosion of metal components by the coolant is undesirable because:

- Penetration of the metal that contains the reactor coolant impairs the system integrity
- Transport and deposition of metallic corrosion products in the core results in activated materials
- Degradation of major piping systems makes it susceptible to leaks and release of radioactivity to the environment
- Deposition of corrosion products on heat transfer surfaces reduces plant efficiency
- Corrosion of fuel cladding would produce a loss of fuel integrity.

Corrosion weakens the structure leading to deterioration. It is especially a problem in a nuclear reactor core. Metals released from welded surfaces of the RCS are subject to activation. The activated corrosion products are dispersed in the coolant and through the reactor coolant system. This is an important contribution to radioactive contamination of the reactor coolant system. Activation of corrosion products yields a number of long-lived energetic gamma emitters (see Table 3.1-1).

In addition to the radioactivity in the coolant, the activated corrosion products plate out on exposed surfaces. This creates radiological exposures and hazardous waste generation. Moreover, the deposition of the corrosion products on heat transfer surfaces reduces heat transfer. In addition, it creates both thermal and radiological hot spots.

Although the materials employed in the coolant system piping and components of a reactor have excellent corrosion resistance, some corrosion does occur. The utility of these materials depends on the development of protective films that retard the rate of attack of the underlying surfaces. In addition to the more uniform corrosion of exposed surfaces, most materials are susceptible to one or more of a variety of forms of local attack. Localized corrosion is usually associated with specific impurities and the ambient conditions of exposure or to the mechanical arrangement of components.

This section discusses the chemistry of corrosion. To simplify the presentation, a PWR is assumed; however, the general principles apply to BWRs. The primary differences are in the selection of materials and the operating/design characteristics of the plant. As shown in subsequent sections of this chapter, these differences significantly affect plant chemistry.

There are several types of corrosion of concern in a nuclear power plant. These mechanisms are summarized in Table 3.1-2 and include:

- General corrosion
- Galvanic corrosion
- Stress corrosion
- Crevice corrosion
- Pitting corrosion

Another mechanism for the loss of material from the exposed surface to the solution is erosion. In erosion induced surface wear, the passive layer (or non-reactive protective surface) is removed by turbulent flow produced by:

- High velocity fluid flow
- Changes in flow cross-section, e.g., smaller piping
- Changes in direction, e.g., elbows, bends
- Changes in flow resistance (e.g., filters, screens)

3.1 GENERAL CORROSION

Direct chemical attack usually results in fairly uniform attack over the entire surface of the metal; it produces a general corrosion that results in relatively uniform removal of materials from all surfaces in contact with the coolant water.

With proper controls, corrosion products are normally released to the RCS at low rates; i.e., in the range of $\text{mg}/\text{cm}^2/\text{month}$. Stainless steel is the most prevalent material in contact with the reactor coolant water. Its corrosion can be illustrated by the corrosion of iron in pure water.

In general, the corrosion rate increases with temperature as the protective film becomes less effective.

Scale formations at low and high temperature are represented in Figure 3.1-2. It shows that for a typical metal, the depth and composition of the scale differs with temperature.

In the RCS, ferrous hydroxide decomposes to form magnetite (magnetic iron oxide), hydrogen and water. The magnetite develops a protective film on material surfaces and provides a barrier between the water and the iron. As the thickness of the film increases, the corrosion rate

decreases. As a result the overall corrosion rates establish equilibrium and are maintained within acceptable values.

The corrosion of metals in the reactor coolant system is of little importance to service life because the overall corrosion rates are very slow and the RCS component walls are thick. General corrosion does not threaten the integrity of the system because its prevention has been emphasized in plant design. However, it is important to the purity of the water and the cleanliness of the system because the corrosion products become waterborne. This occurs by erosion of the protective film.

The corrosion products can be transported to the reactor core region where they are activated by neutron capture. This process results in finely divided corrosion products that include radionuclides formed by activation, called CRUD (Chalk River Unidentified Deposit).

Constituents of crud are frequently released to the coolant in colloidal form (particles < 0.2 micron); i.e., too fine to settle or be readily removed by filtration.

Crud has several undesirable characteristics. For example, it:

- Transports throughout the reactor system
- Fouls heat transfer surfaces
- Collects inside the reactor and becomes activated.

Once specific elements contained in crud are activated by exposure to neutrons in the reactor core, the crud becomes a major contributor to personnel exposure and to radioactive waste inventory.

Over time crud accumulates in coolant and combines into larger particles, which form suspended solids. This slurry-like suspension is unstable. Some of these solids settle in regions of low water velocity. These "crud traps" collect considerable amounts of radioactive crud and produce radiation "hot spots." Figure 3.1-3 provides a simplified model of reactor plant crud buildup.

Fluid velocity, purification practices, bleed and feed operations, chemistry control, and boron-pH relationships affect changes in crud solubility and, therefore, the dynamic deposition-release processes that determine system radioactivity in various parts of the system.

For example, the steady-state concentration of activated corrosion products attained during operation at uniform power levels in a PWR are only 1-10 parts per billion (ppb). However, power transients, shutdown, and startup often produce spikes in excess of one part per million (ppm), which is two or three orders of magnitude greater.

Crud is released from surfaces to which it is adhered to become suspended in the reactor coolant by:

- Chemical shock
- Thermal shock
- Mechanical shock.

If the shock causes a relatively large, rapid re-suspension, it is referred to as a "crud burst".

Chemical shock is a reaction of the RCS corrosion layer resulting from changes in chemical composition of the reactor coolant. For example, an increase in the oxygen concentration or a decrease in pH in the system changes the chemical equilibrium of reduction and oxidation products (redox state).

Thermal shock is a disturbance of the crud layer because of differential expansion and contraction rates between the RCS piping and the crud layer. Reactor heatup and cool down are good examples of this type of shock.

Mechanical shock occurs when movement of RCS components disturbs the crud layer. Examples are the starting and stopping of recirculation pumps or a reactor trip.

Crud bursts often lead to the removal of protective corrosion films that leave fresh metal exposed. This results in additional corrosion and causes RCS activity to abruptly increase.

3.1.1 Corrosion of Iron and Activation

A major source of cobalt-60 is attributable to the corrosion of iron. The release of iron oxide and accompanying ions into the feedwater of a BWR is a good example. In this case, iron oxide released via corrosion is accompanied by the release of divalent cobalt cations.

Iron oxide is the only medium that provides ample residence time of cobalt-59 in a neutron flux to be activated to cobalt-60. Dissolved cobalt adsorbs on the iron oxide and is carried to the fuel surfaces. The oxide adheres to the heated zircaloy fuel rods where cobalt can be activated. The average residence time for iron on the fuel, thus the quantity of cobalt-60- produced, is a function of the quality of iron oxide.

The rate of release of iron oxide particles is dependent on coolant:

- Oxygen content
- Temperature
- Conductivity
- pH

Colloidal iron complexes (particles $<0.2\ \mu\text{m}$) readily pass through clean filters. They deposit on the fuel and adhere tenaciously. This produces high activities of cobalt-60, which in colloidal form is normally not a significant direct contributor to either exposure or waste disposal activity when the fuel remains in the reactor.

Any iron oxide with a particle size between 0.2 and $1.0\ \mu\text{m}$ can also pass through filters and is small enough to adhere to the fuel surfaces by momentum transfer, but with weak bonding. After some residence time on the fuel, these activated particles release to the coolant and are available for deposition on the internal surfaces of the piping and components. This material is also a source of radioactive waste and contaminated leakage.

The iron oxide has greater capacity to hold cobalt when it is deposited on the fuel than when it is in the coolant. This leads to exchange of cobalt between the iron in the coolant and the iron oxide deposited on the fuel. The deposited iron oxide can retain the cobalt long enough for it to be activated.

When released from the fuel, some activated cobalt is carried with iron to the interior surfaces of the reactor coolant system where it is deposited. The iron in solution can circulate and redeposit on the fuel and produce another generation of cobalt-60 production. Repeated cycles increase the specific activity in the water and on the system interior.

If the iron oxide is in particles $>1\mu\text{m}$, such as from erosion or spalling of the surface layer; it creates a sediment, but does not contribute appreciably to cobalt-60 production. However, by abrasion it assists in developing inter-mediate particle size iron oxides.

Some cobalt-60 cations are released to recirculation and absorb on crud in the water. They are transported on the crud to piping and other coolant system surfaces. In addition, some cobalt ions are incorporated into the growing-on corrosion film of the recirculation piping, etc. The corrosion film undergoes active growth and release. Over time some cobalt-60 ions and crud containing cobalt-60 are released to recirculation. Some of this material is removed by water purification and becomes part of the plant radwaste. The remainder recirculates through the reactor system and continues the cycle of deposition, release, incorporation and re-release. This leads to a buildup of cobalt-60 activity in solution unless some equilibrium or quasi-equilibrium state is achieved.

In reactor grade water, the rate of stainless steel corrosion, and uptake of cobalt into the corrosion film, is a linear function of conductivity. Moreover, there is a memory effect because the rate of cobalt uptake is much higher than the release rate. This leads to greater uptake as a result of high conductivity than implied by linearity.

3.1.2 Corrosion Control

The corrosion rate of most materials is related to the following water chemistry characteristics:

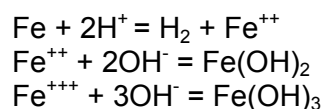
- Oxygen content
- Hydrogen content
- Solution pH
- Temperature
- Presence of inhibitors

3.1.2.1 Oxygen Content

Oxygen control within 20-200 ppb is effective in minimizing general corrosion, but such variability contributes to release of the intermediate range particles of iron oxide from feedwater piping. Therefore, oxygen should be maintained as constant as practicable at or below 50 ppb. At low concentrations of oxygen (< 5 ppb), a very large quantity of ferrous iron is produced. This leads to larger corrosion rates and releases of iron to solution.

When a reactor is shutdown, oxygen contained in the makeup water and shutdown cooling water oxidizes the materials in the surface layer on reactor surfaces. This alters the size, shape, and solubility of these materials. Previously adherent layers become available for transport in the coolant. During operation similar affects can occur.

The basic steps of the general corrosion process are:



This reaction can be stopped or mitigated by:

- Reducing the reactants (Fe and H^+)
- Separating the reactants
- Driving the process in reverse by increasing the reaction by-products

In the absence of oxygen, ferric hydroxide and ferrous hydroxide combine to form a protective film. This physically separates the reactants and reduces further corrosion. The reaction is self limiting. However, if dissolved oxygen is present, the ferrous hydroxide is converted to ferric hydroxide. By itself, ferric hydroxide is not an adherent protective film. Thus, the oxygen must be minimized to limit corrosion. In a PWR, this is done by:

- Maintaining a slight excess of hydrogen
- Adding oxygen scavengers such as hydrazine

Hydrazine is only used during reactor startup because the range of temperature in which it exhibits the appropriate characteristics is limited.

3.1.2.2 Hydrogen Content

Dissolved hydrogen in water is a weak corrosion inhibitor, but the major impact is scavenging oxygen. Hydrogen addition is a long standing practice in PWRs and is now a common practice in BWRs.

3.1.2.3 Solution pH

The corrosion rate of most metals in water with a pH above 7 is considerably less than if pH is below 7. Furthermore, the corrosion films are more adherent at a high pH. As indicated in first reaction shown above, hydrogen can drive the reaction toward acid formation and thus increased corrosion. Higher pH offsets this effect.

3.1.2.4 Temperature

In general, corrosion rates increase with temperature. The protective films become less adherent at higher temperatures.

3.1.2.5 Inhibitors

Corrosion inhibitors are used to reduce corrosion by water in relatively low temperature systems. The component cooling water coolant system uses potassium chromate for corrosion control. This produces an insoluble chromate film on the surface of the iron, which reduces the corrosion rate. Corrosion inhibitors such as potassium chromate are not effective in the reactor coolant system because they decompose under conditions of high temperature and strong radiation flux.

3.2 PWR REACTOR COOLANT CHEMISTRY

Chemistry of the PWR reactor coolant is based on control of:

- Core reactivity
- Corrosion of RCS construction materials
- Fuel cladding integrity

Reactor coolant chemistry maintains water within acceptable specifications for boron, chlorides, fluorides, oxygen and pH. Boron is used for reactivity control; whereas, the other parameters are important to corrosion control. Tech Specs also address limits on iodine.

3.2.1 Chemistry Requirements

Chemical reactions within the RCS that lead to production of activated corrosion products determine the convenience of operation and maintenance, as well as waste disposal requirements. Therefore, even low corrosion rates can be important.

3.2.1.1 Reactivity Control

Boric acid is used to supplement the control rods for reactivity control; therefore, lithium hydroxide is added to control system pH. Boric acid is readily available and is relatively non-corrosive to structural materials used in the RCS under operating conditions.

Boric acid ionization potential varies inversely with temperature. At PWR operating temperatures, it is nearly neutral.

Lithium hydroxide ensures alkalinity through-out the range of temperatures experienced by reactor coolant. The use of boron and lithium compounds can result in production of tritium. To reduce the amount of tritium produced the lithium hydroxide is enriched to 99.9% Lithium-7.

The need to maintain appropriate concentrations of boric acid and lithium also introduces requirements on the reactor coolant purification system. Typically mixed bed resin demineralizers are used to remove contaminants such as fluorides, chlorides, soluble corrosion products, and fission products. Unfortunately, such demineralizers remove lithium and boric acid until the resin is saturated with these ions at which point the demineralizers become transparent to the boric acid and lithium.

3.2.2 Treatment

Treatment of the primary coolant consists of adding:

- Boric acid for reactivity control
- Hydrogen (or hydrazine) for oxygen scavenging
- Lithium for pH control
- Demineralization to remove halides and other contaminants
- Filtration to remove insoluble materials

3.2.2.1 Boric Acid Control

As fuel burnup proceeds during the core cycle, less boron is required for reactivity control. The excess boron is removed periodically by diverting some reactor coolant to the waste system and diluting the coolant with makeup water. Late in core life, boron is removed by anion resin in the letdown system. Some is also removed (or added) by the reactor coolant purification system, which is used for halide control. Boric acid has limited solubility at ambient temperature and is more acidic; therefore, systems or tanks containing saturated boric acid solutions at ambient temperature must be heat traced and the boric acid must be handled with care to avoid corrosion of system components.

3.2.2.2 Oxygen Control

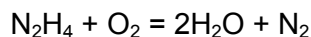
During operations, hydrogen is introduced into the coolant at the volume control tank. It is used to:

- Reduce corrosion
- Suppress dissociation of water into hydrogen and oxygen
- Prevent the formation of nitric acid from nitrogen in the reactor coolant.

Each of these is accomplished by hydrogen's ability to scavenge oxygen.

Hydrogen addition is not an efficient means of controlling oxygen during shutdown or during cool down or heatup. Under these conditions, hydrazine is used for oxygen scavenging. This requires relatively large quantities of hydrazine to offset the large reservoir of dissolved oxygen.

Hydrazine reacts with oxygen according to:



However, hydrazine decomposes at higher temperature and is not effective at operating temperatures.

3.2.2.3 pH Control

Lithium hydroxide, enriched to 99.99% lithium-7, is added via the chemical mixing tank to:

- Control pH of the coolant for corrosion control
- Reduce deposition of corrosion products on heat transfer surfaces.

The pH specification range is 4.2 to 10.5. To accomplish this, lithium concentration is kept between 0.7 and 2.0 ppm. The broad range in acceptable pH results from the large variation in boron requirements throughout core life. It is not practicable to totally compensate for boron throughout core life by adding sufficient lithium hydroxide to buffer the boric acid. A number of factors affect the pH of the coolant. As the temperature of pure water increases, more molecules of water are dissociated into hydrogen ions and hydroxyl ions.

If the pH is measured at higher temperature, the measurement shows a net increase in the hydrogen ions or a lower pH. This is a false indication of pure water being acidic. Therefore, it is important to always measure pH at the reference temperature of 25 °C.

Boric acid in the coolant at room temperature adds hydrogen ions and lowers the pH. As the coolant increases to operating temperature boric acid is less ionized and adds fewer hydrogen ions to the coolant. At reactor coolant operating temperature boric acid contributes little to solution pH. Therefore, the actual pH of the reactor coolant at operating temperatures is well above 4.2.

Lithium hydroxide adds hydroxyl ions to the coolant and raises its pH; thus controlling the coolant pH. This inhibits chloride stress corrosion cracking at temperatures of 150 °F and above. This is the temperature range of concern for chloride induced cracking.

This approach to pH control requires only small quantities of lithium because much of the lithium-7 is supplied when the boron-10 in the boric acid undergoes a neutron-alpha reaction. The lithium-7 concentration is controlled by adding lithium or directing it through a mixed bed demineralizer. The largest LiOH additions are required when new demineralizer resins are placed in operation and after refueling.

New cation resin in the hydrogen form removes lithium until it becomes saturated, which normally requires about 45 days of operation at a half-time of about one-day.

3.2.2.4 Halide Control

Chloride and fluoride are both maintained below 0.15 ppm in the primary system. This is low enough to prevent stress corrosion. This is accomplished by bleed and feed using the CVCS mixed bed resin or deborating resin demineralizers.

3.2.3 Activated Corrosion Product Control

In a PWR that has operated for more than two years, cobalt-60 is the major source of radiation and radioactivity. At equilibrium, the inventory of cobalt in PWR typically is around 600 Ci in the core, 200 Ci in the steam generators, and 60 Ci on the piping. After one year the dominant factor affecting out-of-core deposits is operational chemistry.

Coolant pH is the key operational factor affecting radiation field buildup and transport of crud through the coolant system. An increase of pH from 6.9 to 7.5 dramatically decreases crud transport.

During PWR shutdown, the preferred method of controlling the inadvertent release of radioactive corrosion products into reactor coolant is to force oxygenation of the reactor coolant by hydrogen peroxide addition after shutdown, but before drain down. This causes a controlled crud burst that can be used to clean-up the RCS.

The composition of crud varies depending on location and the base material. Crud on the steam generator tubing is different than the core crud in that it contains about ten times the chromium. The highest activity deposits, per unit area, are on the stainless steel piping, followed by zircaloy in the core. The least occurs on Inconel 600 tubing. Deposits on straight lengths of steam generator tubing are uniformly distributed, but deposits double at the U-bends.

The percentage of cobalt in material descaled from Inconel is many times that of the base metal (this suggests either a preferential release of cobalt or a source other than corrosion).

3.2.4 Shutdown Chemistry

As the temperature of the PWR coolant decreases for shutdown, the coolant pH changes from alkaline to acidic. In addition, radiolytic oxidizing radicals begin to cause a shift in the oxidation-reduction equilibrium of nickel and nickel ferrite and dissolved oxygen increases. Chemical conditions change from a reducing to an oxidizing environment. This results in some increase in crud. The chemistry is modified during shutdown and refueling to address this situation.

To avoid a burst type uncontrolled release to the coolant system and the fuel pit during refueling, hydrogen peroxide is added to the coolant to release the crud containing cobalt and nickel into the coolant for cleanup before refueling.

The PWR coolant is deliberately oxygenated before the system is opened. After the oxygenation causes release of corrosion products to the coolant, the purification system is operated at maximum removal flow rates to remove these corrosion products.

3.2.5 Coordinated Lithium-Boron Chemistry

As noted earlier, the pH of boric acid decreases with temperature; therefore, the amount of lithium hydroxide required to achieve a particular pH in the coolant is a function of temperature.

Studies show that an increase of pH from 6.9 to 7.5 changes the solubility of iron from the nickel ferrite film from a depositing condition to a dissolving condition. This change in solubility inhibits the deposition of corrosion products, such as cobalt-60, on piping and equipment surfaces and enhances their removal by filtration and ion exchange.

To maintain coolant pH at 7.5 requires about three times the lithium hydroxide as at 6.9. Moreover, the inventory of lithium in the coolant to maintain a constant pH is a function of both boron concentrations and temperature. Therefore, it is necessary to coordinate lithium and boron concentrations under all operating conditions throughout a core cycle.

Compared to a constant lithium treatment, the coordinated lithium-boron chemistry results in a thinner core deposit film with lower concentrations of impurity elements (aluminum, calcium, silicon, etc.) and nickel. In other words, the higher lithium concentration lowers radiocobalt generation because it depresses the release of nickel into the coolant. With less nickel available to undergo activation to cobalt, the system radioactivity decreases.

Coordinated lithium-boron chemistry is more sophisticated and more difficult to manage, but is supplanting the older constant lithium practice.

3.3 BWR CHEMISTRY (TRADITIONAL)

Until the last several years, water treatment aspects of a boiling water reactor were similar to those of a modern high pressure power plant in that it relied on the minimum treatment approach. As in a conventional power plant the objectives are corrosion control and prevention of scale on heat transfer surfaces. However, in a nuclear plant the production of radionuclides adds other requirements, not the least of these is prevention of the buildup of radioactivity.

The BWR cycle is based on neutral high purity water chemistry. BWR reactor water is maintained in a high state of purity, without chemical addition, to minimize:

- Corrosion of reactor materials
- Fouling of heat transfer surfaces
- Activation of corrosion products
- Coolant radionuclide levels

Water purification is an important part of plant operations and is done by conventional ion exchange and filtration processes. This purification maintains the required coolant purity and, thus, controls radioactivity in the plant. Conventional chemical parameters are used to provide control.

There is also an emphasis on control of air and water condenser in-leakage and oil egress. Water purity is maintained by limiting corrosion product input to the reactor and by continuous cleanup of the reactor water.

Historically, water treatment was confined to adequate filtration, demineralization, and de-aeration.

The principle emphasis in a BWR system is the removal of impurities from the water cycle rather than treatment of impurities already in the operating system.

Unlike a PWR, no additives were originally used in a boiling water reactor to control pH, oxygen, or reactivity. To compensate for the lack of chemical addition, materials were selected for their low corrosion rates.

Pure, low conductivity water with very low chloride concentrations is the most important criterion. Conductivity and chloride ion content are monitored to detect off-standard water chemistry. This approach does not prevent intergranular stress corrosion cracking (IGSCC) of stainless steel.

In response, to the need to extend the life of recirculation system piping and to further reduce plant radiation exposures to be consistent with the ALARA concept, further steps appeared to be warranted.

In recent years, some BWR plants have converted to hydrogen-water chemistry (HWC) to extend piping life and, in some cases, zinc injection to accomplish the ALARA objective. Hydrogen-water chemistry appears to suppress IGSCC during power operations, but it can increase ambient radiation levels in the vicinity of the turbine. This section discusses both normal BWR chemistry and the supplemental controls for hydrogen-water chemistry, as well as modifications required for cold shutdown.

3.3.1 BWR Cycle

A BWR is a closed cycle water processing plant (Figure 3.3-1) that uses high purity water. Water quality in one part of the system inherently affects water quality in other parts. Much of the corrosion product deposition prevalent in the primary system of PWRs is absent in BWRs because steam rather than pressurized fluid flows through the system downstream of the reactor. However, the jet pumps of BWRs are usually very radioactive and the control rod drives tend to be plated with activated corrosion products and/or leak activated primary water.

3.3.1.1 Hotwell

Condensed steam, called condensate, is collected in the hotwell located below the cooling tubes of the condenser. Possible tube leaks in the condenser can result in circulating water from a nearby waterway entering the hotwell, thus introducing impurities. When the circulating water is seawater, the consequences of a very small condenser tube leak are quite significant; therefore, special precautions are required in seawater cooled plants.

The hotwell is de-aerated to reduce the dissolved oxygen content of the water.

3.3.1.2 Condensate Demineralizer/Polisher

The water flows from the hotwell through a full condensate demineralizer to remove insoluble corrosion products by filtration and dissolved ionic materials (i.e., metals and salts) by ion exchange. This affords limited protection from condenser tube leaks until corrective action is undertaken.

3.3.1.3 Feedwater

The feedwater continuously passes through the feedwater heaters and enters the reactor at a temperature about 380-420° F (This varies depending on specific plant design).

There is no blowdown from the reactor water, except for a very low carryover (< 0.1% with the steam), so the reactor concentrates all of the soluble and insoluble materials that enter it via the feedwater.

3.3.1.4 Reactor Water Cleanup (RWCU) System

The RWCU System removes soluble corrosion and fission products, but has only limited ability to remove insoluble corrosion products, such as cobalt-58 and cobalt-60. Thus, extremely pure feedwater is a necessity. The RWCU filters typically have the highest activity concentration of all the filters utilized in a BWR.

3.3.2 Control of Water Quality

In plants not using hydrogen addition or zinc injection, the primary design basis for the BWR water quality control is to maintain the primary coolant as pure as practicable by a combination of selecting materials having low corrosion rates and the removing of corrosion products that are released into the system. The reasons are:

- Deposition on fuel surfaces retards heat transfer
- Deposition of radioactive activation and corrosion products on system surfaces increases radiation exposure rates and hinders shutdown maintenance
- Corrosion products from material surfaces throughout the coolant system can migrate into the core and become radioactive
- Corrosion products contribute a major portion of radioactivity in most radwaste streams.

Two types of corrosion are of concern in a nuclear power plant. The first is a stress type of corrosion cracking; the second is general corrosion.

The reactor coolant system is built of corrosion resistant materials, primarily stainless steels. These stainless steels have very low corrosion rates, but are susceptible to stress corrosion type cracking. Adherence to special limits for chloride ion concentration is necessary to avoid conditions that could lead to stress cracking.

Other parts of the plant use less corrosion resistant materials, such as low alloy steels in the steam line, turbine and condenser.

The corrosion products released from the large surface areas of these materials must be removed from the feedwater before it enters the reactor vessel. This is necessary to minimize the amount of material carried to the reactor, such material could deposit on heat transfer surfaces of the fuel and foul critical flow areas.

Reducing the amount of material entering the reactor vessel helps to minimize the amount of activated corrosion product (crud) buildup in out-of-core locations of the primary system.

Degradation of carbon steel in plant recirculation piping has become an important concern. There is evidence that addition of hydrogen to the coolant water slows carbon steel corrosion and, thereby, extends the life of plant piping systems.

This led to the adoption of hydrogen water chemistry at BWRs. The hydrogen addition minimizes oxygen and, thereby, reduces corrosion. Monitoring tests indicate that this results in a drastic reduction in the crack rate of recirculation pipe.

Water purity is maintained by:

- Condensate demineralizers
- Reactor water cleanup demineralizers

An undesirable competing mechanism for clean-up is the deposition, or plate-out, of corrosion products on system surfaces. In the reactor core such deposits reduce heat transfer and restrict primary coolant flow. If such deposits remain in suspension, they could be effectively removed by the clean-up system.

To reduce the plate-out of activated corrosion products on the interior surfaces of piping and equipment, some plants rely on zinc injection. Zinc oxide, in a white powdered form, is pumped into the reactor feedwater. As the zinc circulates through the reactor system it deposits in the corrosion film on piping. It provides competition for other metals for a place in the corrosion matrix. As a result, it reduces the buildup of cobalt-60, etc.

The zinc concentration must be maintained within a narrow range to remain effective, yet avoid the production of excessive zinc-65, which is radioactive. Such radioactive zinc would end up in the radioactive waste and would also increase radiation levels in the plant deep-bed condensate polisher.

It is difficult to quantify the zinc-65 in the waste, but it has an advantage of a much shorter half-life than cobalt-60.

Maintenance of high quality water is important during outages and shutdowns as well as during operations, for water is often transferred from one part of the plant to another during outages, and this water can easily find its way to the hotwell and from there to the reactor.

3.3.3 BWR Chemistry Requirements

Pure, low conductivity water with low chloride concentrations is the primary chemistry requirement in a BWR.

The use of a high purity neutral pH water environment in BWRs greatly simplifies and facilitates the monitoring of system chemistry.

The three most important chemical parameters in the chemistry of BWRs are:

- Conductivity
- pH
- Chloride.

3.3.3.1 Conductivity

The reactor water is high purity water and no additives are used for the control of pH. Therefore conductivity is the major criterion of water purity (and indirectly pH). Thus, the primary monitoring parameter is electrical conductivity (specific conductance). Conductivity is defined as the reciprocal of the resistivity. The unit of resistivity is the ohm-centimeter (ohm-cm). The unit of conductivity is mho/cm. The conductance of a solution is proportional to the concentration of ions present. Therefore, any ionic impurities increase conductivity. Because conductivity is very low in a BWR, it is typically expressed in $\mu\text{mho/cm}$.

The normal operating limit for reactor water is 1 $\mu\text{mho/cm}$, at which point the pH is within the range of 5.8 and 8.6. If the conductivity is above the normal operating range of 0.2 to 0.3 $\mu\text{mho/cm}$, either the input is high or the cleanup system is not effective enough for adequate removal of soluble species.

3.3.3.2 pH Control

A second important monitoring parameter is pH, mathematically defined as the reciprocal of the logarithm of the hydrogen ion concentration, or:

- $\text{pH} = -\log [\text{H}^+]$

Neutral water has a pH of 7, derived from the physical fact that, at a given temperature, a finite number of water molecules dissociate into H^+ and OH^- ions. Control of pH minimizes corrosion rates.

The feedwater conductivity approaches the theoretical limit for pure water and there is not normally a need to measure pH. The normal operating limit for the reactor is 1 $\mu\text{mho/cm}$ at which point the pH must be within the range of 5.6 to 8.6. However, if the conductivity is 1.0 μmho , or greater, the pH range expands and should be confirmed.

3.3.3.3 Chloride

Chloride concentration in reactor water is a third major parameter in BWR chemistry. It is also subject to plant technical specifications.

The relationship between chloride and stress type corrosion cracking in stainless steel is well established, and is a very important parameter. The relationship of chloride stress failure is a function of both chloride and oxygen. These effects are shown in Figure 3.3-2.

There is no continuous monitor for chloride so these analyses must be performed in the lab on grab samples.

Chloride concentrations in the feedwater are normally < 2 ppb, which is the lower detection limit of the analytical method. Therefore, any time chloride is measured, it indicates a problem with the ion-exchange resins and warrants investigation without delay. Because the analytical detection level is 2 ppb, chlorides must be measured in reactor water samples rather in feedwater samples.

The normal operating limit for operation is 200 ppb; the absolute maximum limit for chloride is 1000 ppb, or 1 ppm. Operation between 200 ppb and 1000 ppb is restricted to a very limited time.

This limit is based on an oxygen concentration in the reactor water of 0.2 to 0.3 ppm. A level of 1 ppm chloride can be tolerated for short periods. During startups and when steaming rates are less than 100,000 lbs/hr, the oxygen levels in the reactor water can rise to several ppm, and the chloride limit under these conditions is 200 ppb.

3.3.3.4 Other Parameters

Other parameters routinely monitored are:

- Non-soluble impurities (turbidity)
- Oxygen
- Silica
- Boron

Major non-soluble impurities include iron, copper, and nickel. These impurities could plate out on surfaces of the fuel and decrease heat transfer capabilities.

Insoluble iron is sometimes referred to as simply "insoluble" or turbidity. Continuous turbidity instrumentation (turbidimeter) is available to monitor this parameter, but it is generally measured by filtration and laboratory analysis of the filters. Crud levels in the reactor water are usually < 50 ppb; therefore, the reactor water should be clear when sampled.

Increases in turbidity indicate a change in the normal physical processes governing crud behavior; i.e., a scram or major power change. While long-term operation with a high crud level is possible, such levels represent a high input of contaminant or other abnormal situation. It could lead to difficulties with control rod drives or other reactor components.

It is desirable to limit oxygen because of its role in both general corrosion and pitting. Gaseous oxygen is drawn off by the air ejectors, but this doesn't remove dissolved oxygen. Oxygen is monitored in the feedwater by means of a galvanic cell.

Silica is monitored because it is an early indicator of anion demineralizer breakthrough. Silica concentrations in the reactor water have a 5 ppm limit. The behavior of silica in water is not well known, so this limit has been set to minimize the possibility of deposition of silica on surfaces and to keep it out of the turbine.

When silica levels rise, it is a sign the anion resins in the condensate demineralizers, or cleanup systems are becoming saturated with silica. With Powdex cleanup systems, silica levels are measured by automatic analyzers and comparison between the inlet and outlet concentrations determine when the resin precoats should be changed.

Boron is checked to ensure that the Standby Liquid Control System (SLCS) is not leaking. A limit of 50 ppm boron in reactor water has been set to ensure that activity associated with boron in the reactor is insufficient to lead to a change in the void coefficient (The sensitivity of the analytical methods is about 1 ppm and there is no reason for the presence of boron in the reactor water of a BWR).

3.3.4 Chemistry Control

A reactor vessel is the single most important part of the primary system. It is not only where the fuel and other critical components are located, but the highest temperatures in the system are within it. This is where the feedwater, which enters through the feedwater sparger, is converted to steam as it is pumped through the core.

While the primary system contains several thousand pounds of water, this capacity represents only 3-4 minutes worth of steam production. The reactor boils 15 to twenty times this amount in 15-20 minutes. Impurities that are present in the feedwater remain with the liquid phase as steam is generated.

There is negligible carryover in the steam phase; therefore, removal is via the cleanup system. If the cleanup system flow is about 1% of the feedwater flow and the cleanup system is 100% effective, the reactor water concentration of soluble and suspended material increases to 100 times its concentration in the feedwater.

This conclusion holds for true solids such as sodium chloride or sodium hydroxide. As a result, the levels of ionic materials in the reactor water can be measured by conductivity and are related to the input rates.

Corrosion products do not follow the same rule because they do not stay dissolved or suspended in the reactor water. Instead, corrosion products in the feedwater tend to disappear from reactor water rapidly. They are insoluble and over 99% plate out on exposed surfaces of pipes, fuel and other components.

When historically standard BWR chemistry is practiced only about 1% of the input remains suspended long enough to be removed by the cleanup system. This conclusion is modified by zinc injection, which limits the plate out of corrosion products in the system. The crud levels in the reactor water are no indication of the quantity of corrosion products in the system, or of the problems they could cause.

To ensure the quality of feedwater, it must be cleaned prior to entering the reactor vessel. The components responsible for producing high quality feedwater are the condensate demineralizers. Moreover, it is important to limit the buildup of soluble and suspended materials within the reactor vessel. The RWCU system serves this function. Both of these cleanup systems are discussed in this section.

3.3.5 Air Ejectors

Air ejectors play a role in plant chemistry control because they remove gases that are present in the coolant. Main steam is supplied to the air ejectors where its velocity is increased to supersonic speeds after passing through the nozzle. A low pressure area is formed at the discharge of the nozzle. Air and non-condensable gases are drawn into the low pressure area from the condenser. The steam then entrains or traps the air and gases. These entrained gases are carried and mixed with the steam before passing through a diffuser and processed by the augmented off gas system.

3.3.6 Condensate Demineralizers

The primary functions of the condensate demineralizers are to:

- Act as a barrier for the reactor against condenser tube leakage
- Minimize the input of metallic material from the feedwater piping.

Condensate demineralizers are the largest contributor, by volume, of resin radwaste in a BWR.

There are two types of condensate demineralizers (also referred to as condensate polishers). One type uses bead type ion exchange resins, while the other uses powdered resins precoated onto nylon or stainless steel filter elements.

Ion exchange is the basic chemical operation for the removal of soluble chemicals in both types of unit. The resins are composed of reactive sites fixed to a chemical chain structure. For cation resins, the reactive sites are negatively charged radicals that normally loosely hold H^+ ions. In the ion exchange process, the H^+ ions are exchanged for a positive ion. The positive ion adheres more tightly to the resin than the H^+ .

For anion resins, the reactive sites are positively charged radicals that yield a OH^- ion to collect other more reactive negative ions. Thus, if an ionic solution is allowed to flow through a mixed resin bed, both positive and negative ions in the solution are collected by the resin. The resulting H^+ and OH^- then combine to yield pure water.

In addition to the ability of these units to remove soluble materials by ion-exchange to produce low conductivity water, pressure drop across the unit limits the length of their operation. The allowable pressure drop depends on the vendor's design. In deep bed systems the pressure drop is an indication of the amount of crud that has been filtered.

Attention to pressure drops is required to avoid fouling of underdrains and post strainers. Pressure drop is usually the basis for change of precoat on Powdex units.

Deep Bed Demineralizers

In salt water cooled plants intrusion of sodium chloride via condenser tube leaks poses a hazard. The ion exchange capacity of deep beds makes them the preferred system for such plants. Deep bed condensate demineralizer systems are used on all saltwater cooled plants because added ion-exchange capacity is necessary for protection against cooling water leakage. They may also be used on fresh water cooled plants.

The resins are loaded as regenerated mixed resins into spherical or cylindrical tanks, with 150 to 200 cubic foot of resin per tank. A large BWR can have 7 to 12 of these units in service. Thus a large volume of resin is being used all the time. The units are generally sized on the basis of a maximum flow rate of 50 gpm/ft² of resin and a bed depth of 30 inches.

Powdered Resin Filter Demineralizers (Powdex)

Powdex resin units are generally used in freshwater cooled plants. Powdered resin units basically consist of ground up mixed bed resins precoated onto a filter system. The quantity of resin is small compared to a deep bed system. Because their ion exchange capacity is limited, they are not used for feedwater purification at salt water cooled sites. They do, however, afford adequate protection to the reactor from small leaks at freshwater cooled sites.

The advantages of a powdered resin network are:

- Radwaste requirements are lower
- Better filtration capability than the deep bed type
- Afford a great deal of flexibility

The flow rate for these units is limited to about 3.5 gpm/ft² of filter surface. The powdex units must have a tremendous surface area on the filter septums. Only about 0.2 pounds of resin per square foot of area is used, thus, not much resin is in use at any time. They are excellent filters, but are less effective as ion exchangers.

Powdex resins are used once and then are discarded as radwaste.

3.3.7 Reactor Water Cleanup System

The cleanup system works on the bypass principle and is the major method for removal of contaminant materials from the reactor water. It serves as a filter to remove the insoluble suspended solids in the cleanup inlet flow and as an ion exchanger to remove the solubles, such as chloride, silica, iodine and fission products.

The criterion of 0.1 μ mho/cm conductivity in effluent is used to determine the need for changing a deep bed of cleanup resin. The beds usually last between 12 and 18 months if the input rate is low.

When the cleanup flow is about 1% of the feedwater flow, the reactor water is cleaned with a half-life of about 5 hours. Thus, if the conductivity increases due to some upset, it takes several hours to restore it to normal.

3.3.8 Feedwater Heaters

Feedwater from the condensate demineralizers passes through the stainless-steel tube feedwater heaters prior to entering the reactor. However, since this water has been previously degassed in the hotwell and has low oxygen content, the level of corrosion products in the carbon steel piping and the stainless steel heaters is also very low.

3.4 BWR HYDROGEN WATER / ZINC CHEMISTRY

3.4.1 Hydrogen Water Chemistry

The purposes of hydrogen water chemistry are:

- Suppress oxygen in reactor water
- Protect against Intergranular Stress Corrosion Cracking (IGSCC)
- General corrosion control
- Change the characteristics of the corrosion film layer in BWR recirculation piping
- Reduce the oxidation state of chromium

In response to the unacceptable degradation of feedwater piping in BWRs from Intergranular Stress Corrosion Cracking (IGSCC) a number of BWRs are adopting hydrogen water chemistry.

Hydrogen water chemistry implies low dissolved oxygen content coupled with low conductivity. It is generally beneficial to the corrosion performance of BWR materials of construction, particularly IGSCC in welds of Type 304 stainless steel.

Experience in plants with brass condenser tubes that used Powdex in the condensate demineralizers indicates that hydrogen water chemistry also aids in the reduction of out-of-core transfer of cobalt-60.

3.4.2 Protection against IGSCC

Hydrogen water chemistry appears to improve the margin for stress corrosion and corrosion fatigue of carbon and low alloy steels, but has a slight adverse affect on their overall corrosion kinetics.

Under hydrogen water chemistry, the dissolved oxygen in the condensate feedwater decreases below the acceptable value for minimal corrosion of carbon steel piping. At very low levels of dissolved oxygen the protective corrosion film on carbon steel undergoes dissolution and produces accelerated corrosion of the base metal. Therefore sufficient oxygen is added to the condensate system to maintain oxygen between 20 and 50 ppb. The volume of oxygen addition is small.

3.4.3 Corrosion Layer Characteristics

Hydrogen water chemistry provides a reducing environment that lowers the oxidation potential of water and also favors formation of a spinel. This spinel is a thinner more adherent film. However, hydrogen water chemistry appears to have no effect on Co-60 concentrations in the corrosion film of stainless steel.

Historically, the corrosion films on BWR piping are a combination of hematite and spinel oxides. Hematite is an alpha ferric oxide (Fe_2O_3). Spinel is a complex metal matrix with a formula of MOM_2O_3 where "M" is the spinel formula representing various combinations of iron, chromium, nickel, cobalt, manganese, copper and zinc.

Higher fractions of hematite in the corrosion film lead to thicker and less protective oxides. This type of corrosion film tends to increase radiation buildup by permitting more corrosion products to enter solution. This tendency is counter balanced because hematite does not have natural site for

crystal formation by divalent ions, such as cobalt and they have lower cobalt concentrations than corrosion films dominated by a spinel structure. Therefore, buildup of radioactive materials on system surfaces is not controlled solely by oxide layer thickness.

3.4.4 Chromium Control

General corrosion of stainless steel and other metals introduce chromium into the BWR recirculation water. Hydrogen water chemistry changes the oxidation of chromium from Cr^{+3} , which is relatively insoluble, to Cr^{+6} . The (+3) valence state in chromium is relatively stable; whereas, in the (+6) state chromium is soluble and readily forms the chromate anion complex $(\text{CrO}_4)^{-2}$. This leads to a slight increase in conductivity and a slight decrease in pH. Conductivity spikes attributable to soluble chromium occur following shutdown of the hydrogen addition system.

3.4.5 Nitrogen-16

BWR chemistry without hydrogen water control provides oxidizing conditions in the reactor coolant. Under oxidizing conditions, stable oxygen-16 is activated to nitrogen-16 by a neutron-proton reaction. The resulting nitrogen-16 is primarily in the form of soluble nitrates and nitrites with a small amount in the form of volatile ammonia.

Hydrogen water chemistry changes the BWR coolant to a reducing environment. Under reducing conditions, the chemical equilibrium shifts from nitrate/nitrite in favor of volatile ammonia. Nitrogen-16 carryover into the nuclear steam increases by as much as a factor of five at full power; however, this is a plant specific variable and in some plants drops (i.e., post-hydrogen water chemistry levels of nitrogen-16 carryover is only 15% of the prehydrogen water chemistry level). However, in such plants a modest increase in hydrogen addition can result in substantial increases in nitrogen-16 carryover. The carryover of nitrogen-16 results in significantly increased dose rates in the turbine building during plant operation from the 6.1 and 7.1 MeV gamma photons produced during radioactive decay. During outage, the dose rate from nitrogen-16 is not a factor since it is no longer being produced and it has a very short half-life of only 7.1 seconds.

3.4.6 Zinc Injection

Studies have shown that zinc injection reduces soluble cobalt-58 and cobalt-60 in the reactor coolant. This occurs because the zinc-enriched corrosion film on the fuel decreases the deposition rate of cobalt and thus less is activated.

The lowest radiation fields in BWRs tend to be in plants that use alloys for condenser tubes and have less efficient filter/demineralizers (e.g., powdered resin). Admiralty brass used in these condenser tubes contains approximately 25% zinc. Powdered resin demineralizers remove only 90% of the ionic impurities; whereas, deep bed demineralizers used at other plants are 99% effective. Therefore, in plants using full bed demineralizers, more zinc from the admiralty brass is removed from the coolant.

The Electrical Power Research Institute (EPRI) conducted studies to evaluate the use of zinc to control BWR radiation field buildup. Tests conducted as part of this study found that under normal BWR water chemistry conditions low concentrations (10-15 ppb) of ionic zinc in the reactor water reduced the buildup of cobalt-60 substantially (by a factor of 3 to 20). The effect is greater under hydrogen water chemistry.

To confirm test study results, EPRI conducted loop testing and sponsored a full scale demonstration/application test of the combined use of hydrogen water chemistry and zinc injection at JAF, which was the first BWR to implement both hydrogen water and zinc injection.

3.4.6.1 Effect On Corrosion Layer Characteristics

The presence of zinc in the reactor coolant increases the spinel fraction in oxide formations on stainless steel. Spinel is a thinner (by a factor of six or more) more protective film oxide. The corrosion protection provided by spinel film is greater than that provided by divalent cations commonly found in a BWR. Furthermore, the zinc competes with cobalt for available crystal lattice sites in the spinel and, under hydrogen water chemistry, it is the dominant divalent ion in the crystal matrix of the spinel; thereby minimizing Co-60 buildup.

Less zinc is necessary for effective protection of Type 304 stainless steel than for Type 306. The zinc pacified layer provides temporary protection, but this protection is not sustained over long periods unless ionic zinc is continuously present in the water.

3.4.6.2 Treatment Process

Zinc injection is initiated in two phases. The first phase covers a preconditioning period in which the zinc-enriched corrosion film is produced. Once this layer is formed, the rate of zinc injection can be reduced to maintain it. Zinc is added as a zinc oxide slurry. In some cases the first phase is not required.

Continuous zinc injection is required to maintain the benefit over a long-term; however, the zinc addition rate is lower after formation of the initial passivation layer. The only significant negative impact observed is an increase of about 5-10% in the zinc-65 content of radwaste. Zinc injection appears to act synergistically with hydrogen water chemistry to reduce cobalt-60 buildup.

Iron, nickel and cobalt form cation deficient oxides and create defects in the crystal lattice that permit other cations to migrate within the oxide. This migration plays a key role in the formation of new cations at the metal-water interface and leads to oxide. It is hypothesized that the excess of zinc ions in a mixed metal oxide migrate to the vacant defect sites and block ion migration by other ions. This produces a quasi-stoichiometric oxide that is highly protective to the base metal.

3.4.6.3 Zinc Activation

About 48% of natural zinc is stable zinc-64, which undergoes activation in the core to yield radioactive zinc-65. Zinc-65 decays with a half-life of 244 days via electron capture and positron emission. About 50% of the decays produce a 1.1 MeV gamma. Most of the zinc that is added to the reactor coolant deposits on the in-core surfaces. Since zinc incorporates into the iron based corrosion product film and the major source of iron in the corrosion product is from the carbon steel feedwater system, controlling the amount of iron entering the reactor coolant from the feedwater system is key to controlling the zinc deposition rate on the fuel surface. Iron reacts with the zinc to form an insoluble complex. Therefore zinc addition in the feedwater is increased in plants with high iron concentrations in the reactor coolant to maintain the desired level of soluble zinc in the reactor coolant.

3.4.6.4 Impact on Radwaste Activity

Because nearly all of the zinc-65 is removed from the coolant water by the Reactor Water Cleanup (RWCU) System during power operation, zinc-65 is a concern for solid radwaste management. Dose rates on the condensate demineralizer ion exchange beds are increased by more than an order of magnitude as a result of zinc-65 removal. To offset this increase in radwaste activity, BWRs attempt to hold materials for a couple of half-lives.

3.4.6.5 Use of Depleted Zinc Oxide "DZO"

One method being used to reduce the production of Zn-65 is the use of "depleted" zinc oxide (DZO). By reducing the concentration of Zn-64, the parent of radioactive Zn-65, the production of this radionuclide may be reduced. DZO has a Zn-64 concentration of 1% from the natural zinc oxide (NZO) value of 48%. Shutdown dose rates at units using zinc are a factor of about 2.5 times lower than other units. At units which have used NZO and have changed to DZO, the most significant drop in Zn-65 level occurs following refueling. Very low dose rates and negligible concentrations of Zn-65 have been measured at units using DZO that have not previously used NZO.

Table 3.1-1: Corrosion Products Typically Found in Reactor coolant

<u>Element</u>	<u>Nuclide</u>	<u>Half-Life</u>	<u>Origin</u>
Manganese	Mn-54	303 days	Fe-54 and a small of Mn-55 in stainless steel and inconel.
	Mn-56	2.58 hours	Fe-56 in stainless steel and inconel.
Iron	Fe-55	2.60 years	
	Fe-59	45 days	Fe-58 in stainless steel and inconel and impurities in feed.
Cobalt	Co-58	71 days	Ni-58 in stainless steel and inconel.
	Co-60	5.26 years	Ni-60 in stainless steel and inconel; Co-59 in stellite.
Nickel	Ni-65	2.56 hours	Stainless steel and inconel.
Chromium	Cr-51*	27.8 days	Cr-50 in stainless steel and inconel.
Zirconium	Zr-95	64.03 days	Zr-94 in zircaloy.
Silver	Ag-110m**	253 days	Ag-109 in control rods.
Tungsten	W-187	23.9 hours	W-186 in stellite.

* Presence in reactor coolant is directly related to the corrosion rate.

** Indicator of control rod cladding failure.

Table 3.1-2: Summary of Types of Corrosion

<u>Type of Corrosion</u>	<u>Susceptible Material</u>	<u>Required Agents</u>
General Corrosion	Most Materials	Accelerated by low pH, high temperature, high oxygen concentration
Chloride Stress	Austenitic Stainless Steel	Chlorides, oxygen, tensile stress, high temperature
Fluoride Stress	Zircaloy, Inconel	Fluoride, oxygen, tensile stress, high temperature
Caustic Stress	Zircaloy, Austenitic and Ferritic Steels	High pH at point of attack
Crevice Corrosion	Most Materials	Crevice, oxygen, salts in water
Galvanic Corrosion	Most Materials	Dissimilar metals, electrolytes, conducting solutions
Pitting	Ferritic Alloys	Chlorides, oxygen
Hydrogen Embrittlement	Zircaloy, High-strength Steels	Hydrogen
Lead Stress	Inconel	Lead in water

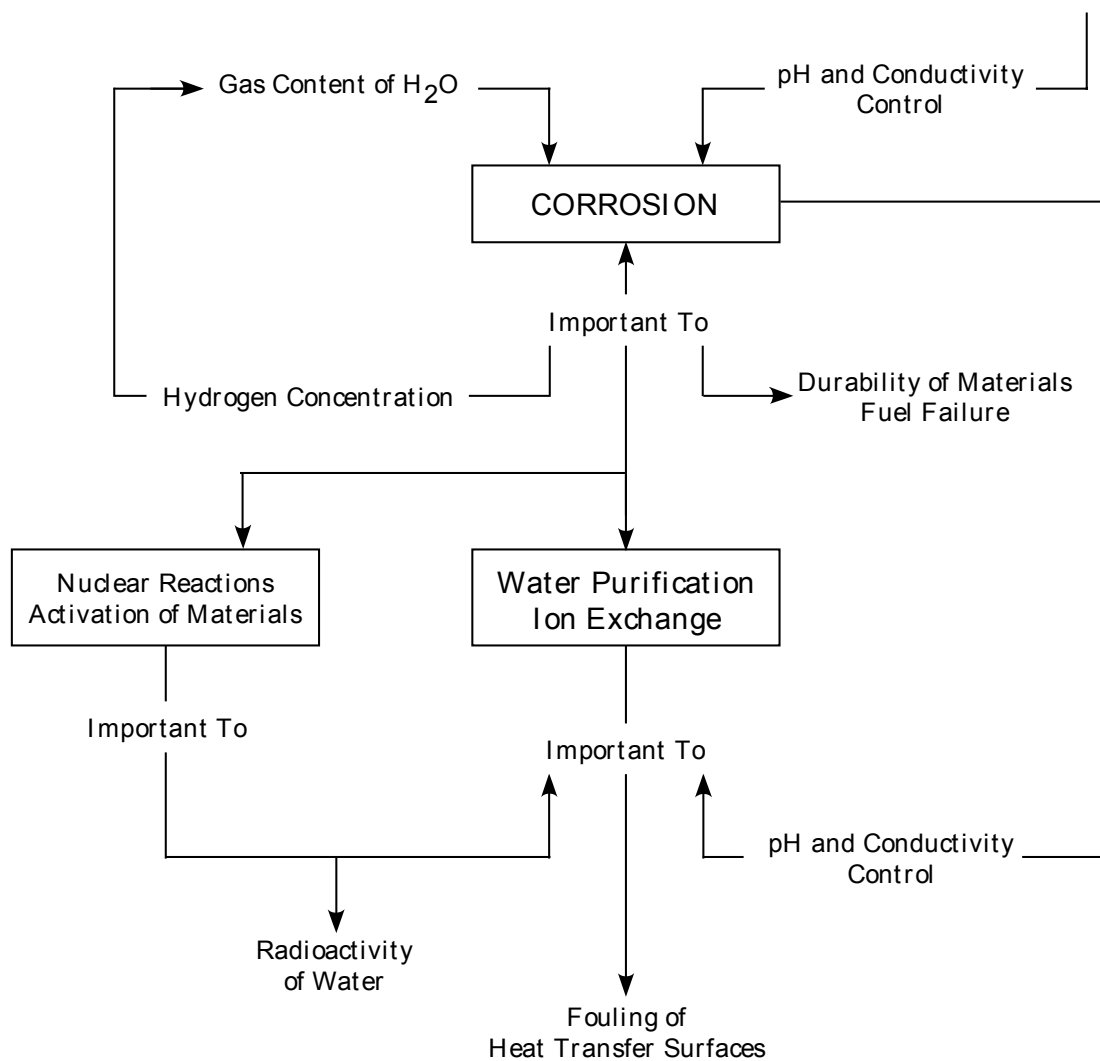


Figure 3.1-1 Interdependence of Chemistry and Corrosion

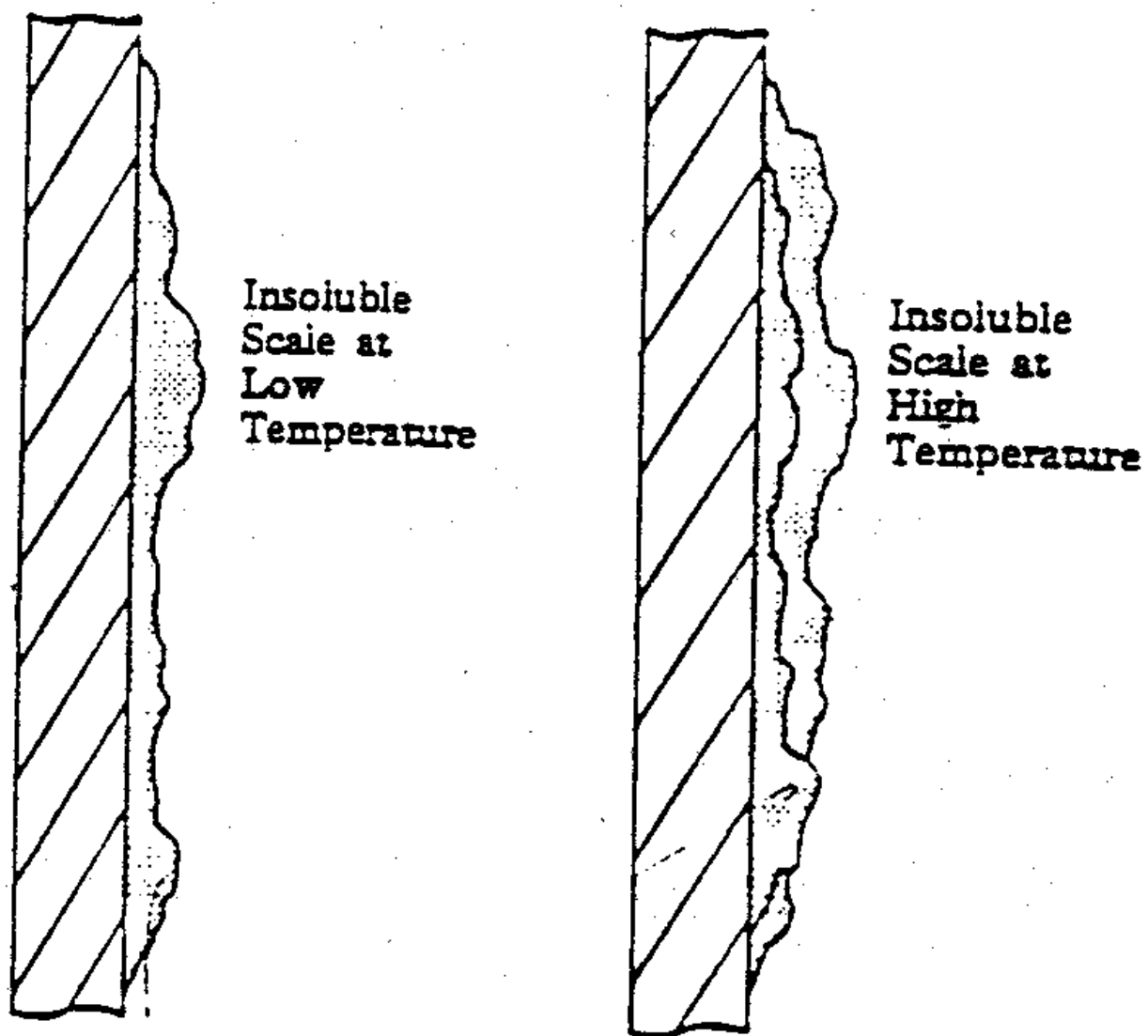


Figure 3.1-2 Generic Representation of Scale Formations at Different Temperatures

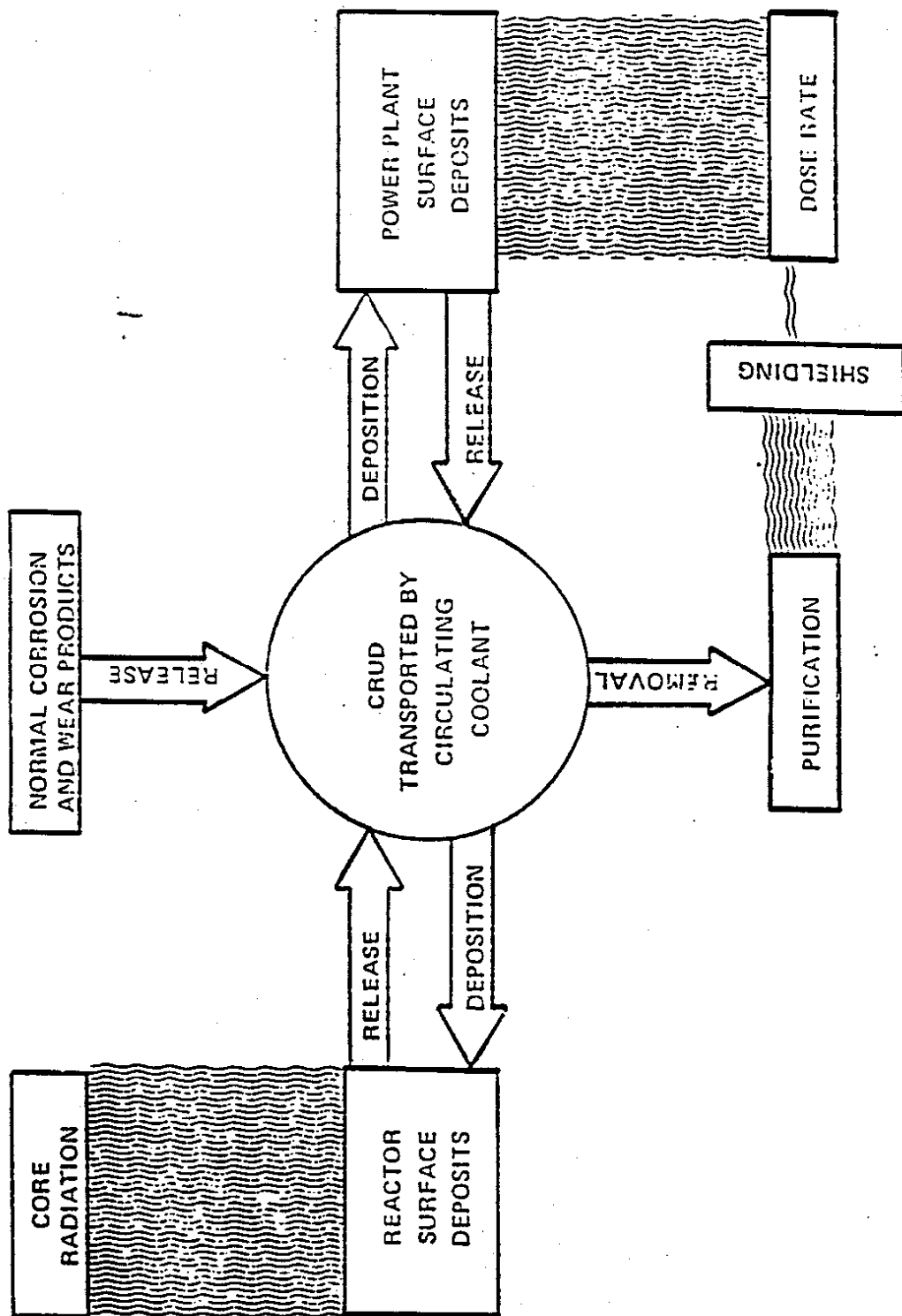


Figure 3.1-3 Simplified Model of Reactor Plant Crud Buildup

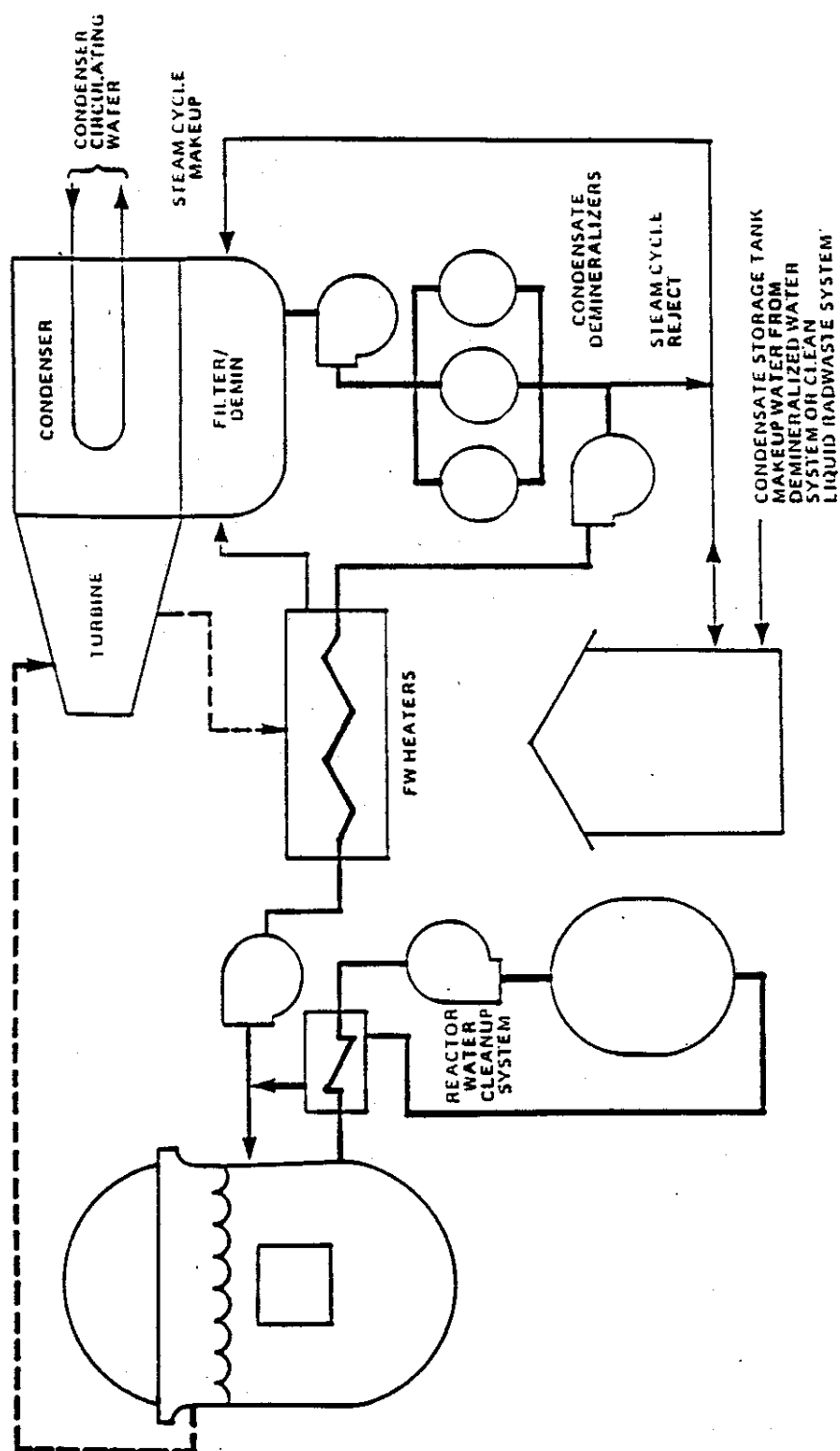


Figure 3.3-1 BWR Water Cycle

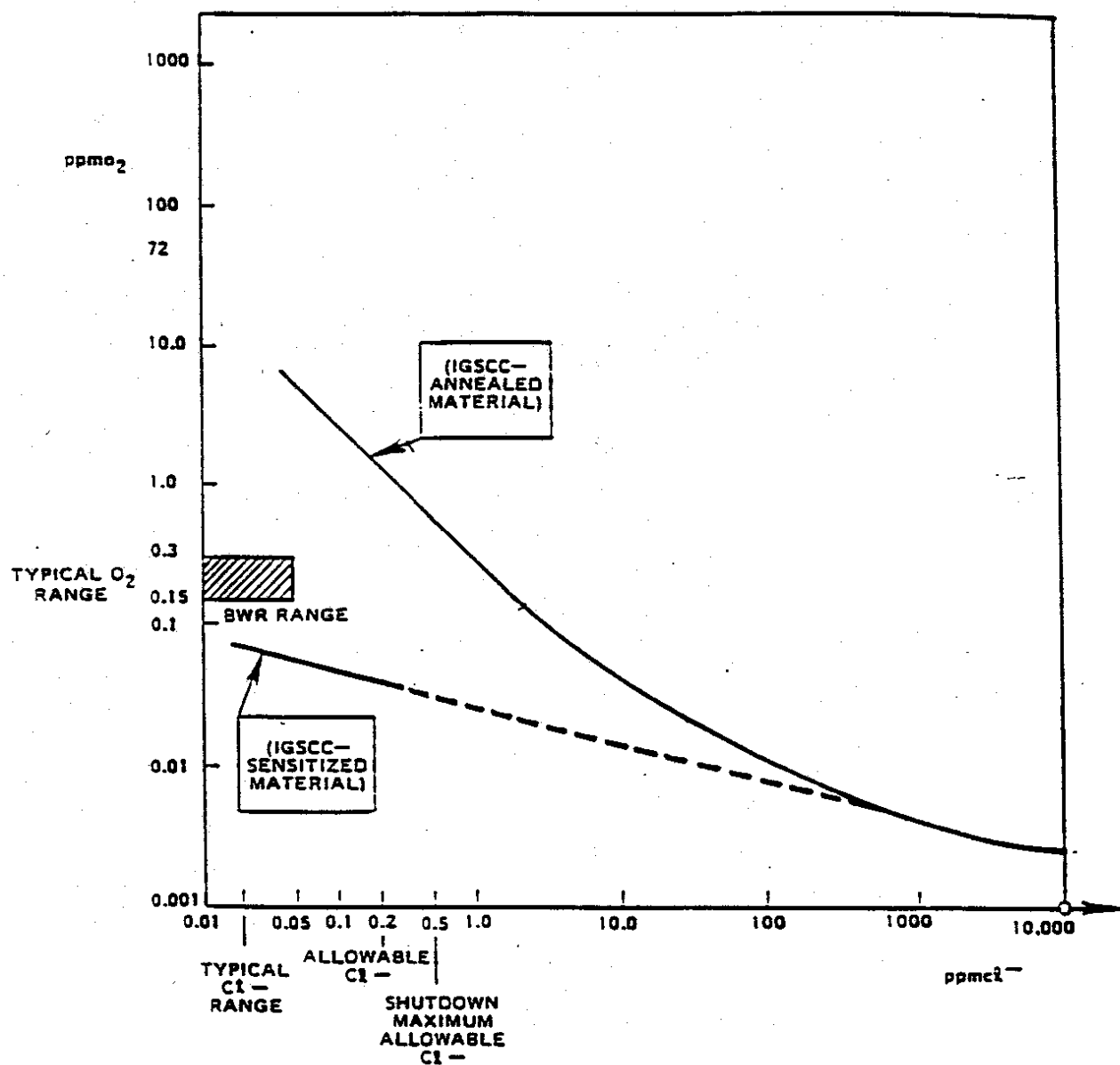


Figure 3.3-2 The Effects of Oxygen and Chloride on Stress Corrosion Cracking of Austenitic Stainless Steel in High Temperature Water

MAJOR ACTIVATED CORROSION PRODUCTS IN LIGHT WATER REACTORS

Nuclide	Half-Life	Formation Reaction	Nature Isotopic Abundance (%)	Activation Cross Section (Barns) ^a		
				Thermal	Epithermal	Fast
⁵¹ Cr	27.7 d	⁵⁰ Cr(n,γ) ⁵¹ Cr	4.35	16.0	0.68	
⁵⁴ Mn	312.2 d	⁵⁴ Fe(n,p) ⁵⁴ Mn	5.8			0.11
⁵⁶ Mn	2.58 h	⁵⁵ Mn(n,γ) ⁵⁶ Mn	100	13.3	1.13	
⁵⁵ Fe	2.73 y	⁵⁴ Fe(n,γ) ⁵⁵ Fe	5.8	2.5	0.1	
⁵⁹ Fe	44.51 d	⁵⁸ Fe(n,γ) ⁵⁹ Fe	0.3	1.14	0.1	
⁵⁸ Co	70.88 d	⁵⁸ Ni(n,p) ⁵⁸ Co ^b	68.3			0.146
⁶⁰ Co	5.27 y	⁵⁹ Co(n,γ) ⁶⁰ Co	100	37.5	6.05	
⁶³ Ni	100 y	⁶² Ni(n,γ) ⁶³ Ni	3.6	14.6	0.77	
⁶⁵ Ni	2.52 h	⁶⁴ Ni(n,γ) ⁶⁵ Ni	0.9	1.50	0.07	
⁶⁴ Cu	12.7 h	⁶³ Cu(n,γ) ⁶⁴ Cu	69.2	4.4	0.40	
⁶⁵ Zn	243.8 d	⁶⁴ Zn(n,γ) ⁶⁵ Zn	48.6	0.82	0.13	
⁷⁶ As	26.3 h	⁷⁵ As(n,γ) ⁷⁶ As	100	4.4	5.08	
⁹⁵ Zr	64.02 d	⁹⁴ Zr(n,γ) ⁹⁵ Zr	17.4	0.075	0.031	
^{110m} Ag	249.8 d	¹⁰⁹ Ag(n,γ) ^{110m} Ag	48.17	4.7		
¹¹³ Sn	115.1 d	¹¹² Sn(n,γ) ¹¹³ Sn	1.01	0.71	2.2	
¹²⁴ Sb	60.2 d	¹²³ Sb(n,γ) ¹²⁴ Sb	42.7	4.0	9.7	
¹⁸¹ Hf	42.4 d	¹⁸⁰ Hf(n,γ) ¹⁸¹ Hf	35.2	12.6	2.26	
¹⁸² Ta	114.43 d	¹⁸¹ Ta(n,γ) ¹⁸² Ta	100	22.0	56.4	
¹⁸⁷ W	23.9 h	¹⁸⁶ W(n,γ) ¹⁸⁷ W	28.6	37.2	33.9	

^aData for 20°C.^bBurnup cross section, σ_b, for Co-58 is 1.9x10⁻²¹ cm².

Table 3.1-3 Major Activated Corrosion Products

**SELECTED ANS STANDARD RADIONUCLIDE CONCENTRATIONS IN REACTOR
COOLANTS - FISSION PRODUCTS ($\mu\text{Ci/kg}$) (Ref. 7)**

Nuclide	BWR ^a		PWR ^b	
	Reactor Water	Steam	Reactor Water	Secondary Coolant
Kr-85m	—	1.0		
Kr-85	—	0.004		
Kr-87	—	3.3		
Kr-88	—	3.3		
Kr-89	—	21		
Xe-133m	—	0.049		
Xe-133	—	1.4		
Xe-135m	—	4.4		
Xe-135	—	3.8		
Xe-137	—	26.		
Xe-138	—	15		
I-131	2.2	0.033	45	0.0018
I-132	22	0.33	210	0.0031
I-133	15	0.23	140	0.0048
I-134	43	0.65	340	0.0024
I-135	22	0.33	260	0.0066
Rb-89	5	0.005	190	
Cs-134	0.03	—	7.1	
Cs-136	0.02	—	0.87	
Cs(Ba)-137	0.08	—	9.4	
Cs-138	10	0.01	—	
Sr-89	0.1	—	0.14	
Sr(Y)-90	0.0007	—	0.012	
Sr-91	4	—	0.96	
Sr-92	10	—	—	
Y-91	0.04	—	0.0052	
Zr(Nb)-95	0.0008	—	0.39	
Mo(Tc)-99	2	—	6.4	
Ru(Rh)-103	0.02	—	7.5	
Ru(Rh)-106	0.003	—	90	
Te-132	0.01	—	1.7	
Ba(La)-140	0.4	—	25	
Ce-141	0.03	—	0.15	
Ce-144	0.003	—	4	
Np-239	8	—	2.2	

^aA reference BWR is a 3400 MWt BWR/5.

^bA reference PWR is a 3400 MWt PWR with U-tube steam generators.

Table 3.1-4 Radionuclide Concentrations in Reactor Coolants - Fission Products

TYPICAL BWR NUCLIDE CONCENTRATION BY WASTE STREAM ($\mu\text{Ci}/\text{cm}^3$)
 (Reproduced with Permission, EPRI NP-5983, Ref. 2)

Nuclide	RWCU Resins	Condensate Resins	Radwaste Resins	Evaporator Bottoms	DAW ^c
Co-60	25.0	2.6	11.2	3.4	4.0E-3
Cs-137	14.1	1.1	6.1	1.9	1.6E-3
Ni-63	3.6E-1	2.3E-1	1.1E-1	1.2E-1	1.0E-4
Fe-55	10.6	2.5	1.3	2.2	4.6E-3
C-14	3.7E-3	7.7E-3	4.6E-3	4.6E-4	2.6E-6
I-129	3.6E-5	3.7E-5	3.0E-5 ^a	3.0E-5 ^a	1.6E-7
Tc-99	5.6E-4	2.3E-4	2.4E-4 ^a	7.6E-5 ^a	1.8E-7
Sr-90	4.5E-2	4.9E-2	1.8E-6	5.6E-2	3.2E-5
Pu-241 ^b	8.5	3.0	7.8E-1	6.7	8.8E-6
Cm-242 ^b	1.2E-1	4.1E-2	1.1E-2	9.3E-2	2.4E-7
TRU ^b	1.5E-1	5.2E-2	1.4E-2	1.2E-1	2.4E-7

a. Values derived from Cs-137 concentrations multiplied by industry-wide scaling factors.

b. Concentration units for these nuclides are nCi/g.

c. DAW = dry active waste; concentrations are based on contact dose rates of 10mR/h.

Table 3.1-5 Typical BWR Nuclide Concentrations by Waste Stream

TYPICAL PWR NUCLIDE CONCENTRATIONS BY WASTE STREAM ($\mu\text{Ci}/\text{cm}^3$)
 (Reproduced with Permission, EPRI NP-5983, Ref. 2)

Nuclide	Primary Resins	Primary Filters	Non-Primary Resins	Non-Primary Filters	Evaporator Bottoms	DAW ^c
Co-60	50	247	3.1	32.0	5.3E-2	2.6E-3
Cs-137	51.0	–	8.41	–	3.5E-2	2.0E-3
Ni-63	16.1	76.2	1.8	18.0	1.1E-1	1.14E-3
Fe-55	5.5	250	3.6	26.5	5.2E-2	7.25E-3
C-14	6.2E-2	1.4	3.1E-2	5.5E-1	1.0E-3	3.25E-5
I-129	1.7E-4	–	6.1E-5	–	4.0E-7 ^a	1.3E-7
Tc-99	6.6E-4	–	1.8E-4	–	4.0E-6 ^a	9.0E-8
Sr-90	1.9E-1	1.4E-1	1.4E-2	1.8E-2	7.7E-5	5.4E-6
Pu-241 ^b	1400	3822	94	289	9.4E-1	6.2E-5
Cm-242 ^b	19.4	53	1.3	4.0	1.3E-2	9.4E-7
TRU ^b	25	68	1.7	5.1	1.7E-2	1.6E-6

- a. These values were derived by applying industry scaling factors to the cesium-137 concentrations.
- b. The unit of concentration for these nuclides is nCi/g.
- c. DAW = dry active waste; concentrations are based on contact dose rates of 10 mR/h.

Table 3.1-6 Typical PWR Nuclide Concentrations by Waste Stream